

Patented June 5, 1928.

UNITED STATES PATENT OFFICE.

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PRODUCING CORROSION-RESISTANT SURFACES ON METALS.

No Drawing.

Application filed March 17, 1926. Serial No. 95,470.

The invention is a process for producing by cementation alloyage a corrosion-resistant surface on an article composed of a corrodible metal or alloy, and the invention also includes articles made by such a process. The term "corrosion-resisting" as used herein refers to the ability to resist the attack of corrosive agents whether normally gaseous, liquid or solid. Examples of gaseous corrosive agents are oxygen-containing mixtures and products of combustion. These often carry water vapor or suspended particles of liquid or solid corrosive substances which render them even more destructive. The commonest liquid corrosive agents are solutions of reactive chemical compounds such as acids. The absorption of carbon by metals is for the purposes of this application to be considered as a type of corrosion. Iron and steel have but slight resistance against the attacks of any of these classes of corrosive agents yet they have such outstanding advantages in other directions that their use is far more wide-spread than that of any other metals. A primary object of the invention is to render iron and steel resistant to corrosion by providing them with a protective casing of the kind referred to, and especially to treat iron and steel so as to render them resistant to the action of oxidizing gases at elevated temperatures.

Cementation processes wherein a chemical element is caused to diffuse into a mass of metal at temperatures below the melting points of the metal and the diffusing element have been studied. The processes commercially known as "sherardizing" and "calorizing" are of this type, zinc and aluminum being the metals which are respectively caused to diffuse in these processes. It has also been proposed to pack iron articles in powdered chromium and then to apply heat to cause the chromium to form a superficial layer of cementation alloy with the iron.

In the process last referred to, which is usually called "chromizing", the temperature required is above 1300° C. and is so high that the chromium, presenting a large surface because of its powdered condition, becomes superficially oxidized in any usual atmosphere, such as one containing products of combustion, and thus loses in a large measure its power to diffuse into the metal to be cased. For this reason it is necessary to maintain an atmosphere of inert gas such

as hydrogen about the powdered chromium, and this again makes it practically imperative to employ electrical heating.

I have discovered that the presence of a content of silicon in the cementation mixture will considerably depress the temperature at which the diffusion takes place, and that the temperature can be so lowered when operating in this way that the chromium is not detrimentally oxidized by such gas mixtures as air or products of combustion. It may be that the presence of silicon directly diminishes the oxidizability of the chromium to some degree, but however this may be the net result is that an inert atmosphere becomes unnecessary. Heating by the combustion of gas or other fuel thus becomes practicable. Electrical heating can of course be used if preferred and an inert atmosphere can be maintained.

The silicon is preferably introduced into the material as an alloy, and it is advantageously alloyed with the chromium contained in the mixture. A ternary alloy of iron, chromium, and silicon possesses certain advantages as the cementation material. It is cheaper than the binary alloy of silicon and chromium and also appears to act more rapidly and effectively. An important advantage over processes using powdered chromium follows the use of silicon alloys since the latter are brittle and easily powdered while the making of chromium powder is quite difficult.

The cementation mixture preferably contains in addition to the active agent or agents a diluent, such as an inert oxide. Excellent results have been obtained with alumina, which has previously been used in processes of this type, but various other oxides and inert powdered materials can be used. A principal purpose of the diluent in the present process is to restrict the rate at which the cementation material enters the surface of the article to be cased so that this rate does not too greatly exceed the rate at which the material penetrates toward the interior of the article. Otherwise there may be too much accumulation of silicon at the surface of the article, producing an alloy of low melting point which will undergo incipient fusion, especially at edges. The proportion of diluent to active material may vary rather widely. Good results have been obtained with the diluent varying from one-

fourth to three-fourths of the total mixture. The best results thus far obtained have been with about 55% of powdered ferrochrome silicon and about 45% of powdered alumina.

5 When the cementation material is an alloy of silicon and chromium, with or without iron, the silicon content may vary widely, for example from 5% to 50% or more. As the silicon content is diminished the rate of diffusion of the cementation material is
10 decreased and it becomes necessary to use higher temperatures or longer times to obtain a case of the desired properties. With increasing silicon there is an increased tendency
15 for an effect already referred to, viz fusion at the surface of the article under treatment.

Temperatures above 900° C. may be employed and it is usually unnecessary to raise
20 the temperature above 1200° C. Between 1100° C. and 1150° C. the alloyage proceeds rapidly but at an easily controllable rate, and this temperature range is preferred. At the temperatures suitable for use silicon
25 has a stronger tendency to diffuse into steel than does chromium. Therefore, if a cementation mixture is used which contains as much silicon as chromium the penetrated
30 portion of the steel will contain more silicon than chromium. For some purposes this is undesirable. For example when the article is being treated to adapt it to resist
oxidation at high temperatures a high chromium content in the coating is desirable.
35 This can be brought about by increasing the chromium: silicon ratio in the cementation material. Thus, when a steel article was treated at 1100° C. with a ferrochrome silicon
containing approximately 40% each of
40 silicon and chromium, there was five or six times as much silicon as chromium in the surface layer of the treated article. With a ferrochrome silicon containing about 8% of silicon and about 60% of chromium, these
45 two elements diffused in nearly equal proportions, but a temperature of 1175° C. was needed to bring about an acceptable rate of action. A protective layer in which the chromium: silicon ratio was sufficiently high
50 was obtained with ferrochrome silicons containing 15% to 20% of silicon and about 55% chromium, and in this case a temperature of 1130° C. was sufficient.

The cementation mixtures may be used
55 definitely if they are periodically replenished in the constituents which have been removed from them. In many instances a casing about 0.03 inches in thickness is desired and this may usually be produced in
60 from three to ten hours. The size of the article treated is not materially changed during the process. There is nothing critical about the degree of fineness in which the materials of the cementation mixture are ap-

plied. Material which will pass a 30 mesh
65 sieve or even coarser material may be used though in most of my experiments the material has been crushed and ground to pass a 60 mesh sieve.

The invention is by no means restricted to
70 the introduction of chromium into the article treated as numerous other metals may be introduced simultaneously or instead of the chromium. The latter metal excels in
75 its ability to diminish oxidation at elevated temperatures and it is therefore of special importance. Silicon alloys are in general
resistant to acids and other chemicals and a sufficient silicon content generally dimin-
80 ishes the tendency of a metal to take up carbon. These effects are added to the effect of the chromium in reducing oxidation or to the specific effect of any other metal used with or instead of chromium.

Where it is desired to augment the resist-
85 ance to acid attack, carbonization or other special form of corrosion, other elements known to be effective for such purposes when alloyed with silicon, for example manganese, nickel, zirconium, titanium and tungsten,
90 may be introduced, the chromium being retained or not depending on the particular purpose in view. The silicon facilitates the diffusion of these other metals in much the
95 same way that it does with chromium, in addition to contributing its own characteristic effect to the superficial alloy.

The casings or coatings formed by the
invention are remarkably adherent. When
100 subjected to deformation sufficiently severe to crack them, the cracks are normal to the surface and there is but little tendency for the case to flake off.

I claim:

1. Process of forming on a ferrous article a
105 corrosion-resisting integral case of predetermined composition containing chromium and silicon, which comprises applying to the article an excess of powdered ferrochrome-silicon having a higher chromium-to-silicon
110 ratio than is to be present in the case, and thereafter maintaining the article in contact with the ferrochrome silicon at a cementing temperature until the article is effectively
115 cased.

2. Process of forming on a ferrous article a corrosion-resisting integral case of predetermined composition containing chromium and silicon, which comprises applying
120 to the article an excess of powdered material having a higher chromium-to-silicon ratio than is to be present in the case, and thereafter maintaining the article in contact with said material at a cementing temperature until the article is effectively cased.
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In testimony whereof, I affix my signature.

FREDERICK M. BECKET.